

Strong coupling of Sm and Fe magnetism in SmFeAsO as revealed by magnetic x-ray scattering

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The magnetic structures adopted by the Fe and Sm sublattices in SmFeAsO have been investigated using element specific x-ray resonant and non-resonant magnetic scattering techniques. Between 110 and 5 K, the Sm and Fe moments are aligned along the c and a directions, respectively according to the same magnetic representation Γ_5 and the same propagation vector $(1\ 0\ \frac{1}{2})$. Below 5 K, magnetic order of both sublattices change to a different magnetic structure and the Sm moments reorder in a magnetic unit cell equal to the chemical unit cell. Modeling of the temperature dependence for the Sm sublattice as well as a change in the magnetic structure below 5 K provide a clear evidence of a surprisingly strong coupling between the two sublattices, and indicate the need to include anisotropic exchange interactions in models of SmFeAsO and related compounds.

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I. INTRODUCTION

Following the discovery of superconductivity in LaFeAsO_{1-x}F_x, with $T_c = 26$ K,¹ an increase of the superconducting transition temperature to above 50 K has been achieved by replacing La with rare-earth (R) elements.²⁻⁶ The highest transition temperature is observed in SmFeAsO_{1-x}F_x ($T_c \sim 55$ K). Interestingly, several studies on powder samples indicate that Sm magnetic order coexists with superconductivity over a range of fluorine doping.⁷⁻⁹ Muon-spin relaxation measurements on R FeAsO ($R = \text{La, Ce, Pr, and Sm}$) compounds found considerable interaction between the rare-earth and Fe magnetism below the ordering of Fe moments ($T \sim 140$ K) only in CeFeAsO.¹⁰ This leads to the conclusion that the R -Fe interaction may not be crucial for the observed enhanced superconductivity in R FeAsO_{1-x}F_x. Recent neutron scattering measurements on NdFeAsO also found an interaction between the two magnetic sublattices, however at $T \sim 15$ K, much below the ordering temperature of the Fe moments.¹¹ In the case of EuFe₂As₂,^{12,13} the only known rare-earth containing member of the A Fe₂As₂ ($A = \text{Alkaline earth, rare-earth}$) family, no interaction has been found so far. Therefore, elucidating the interaction between the two sublattices and determining its nature is an important endeavor in understanding magnetism and superconductivity in the R FeAsO family.

Due to the strong neutron absorption of Sm, the magnetic structure determination in SmFeAsO via neutron diffraction

is considerably more challenging than of other members of the new superconductors. The only attempt was made on a powder sample.¹⁴ Here we report on the first element specific x-ray resonant magnetic scattering (XRMS) and non-resonant x-ray magnetic scattering (NRXMS) studies of SmFeAsO to explore the details of the magnetic structure of the parent compound and to determine the interaction between the two magnetic sublattices. Our resonant scattering experiments show that there is a strong interplay between Fe and Sm magnetism. Magnetic order of Sm exists at temperatures as high as 110 K and can be explained by the coupling between Sm and Fe magnetism.

II. EXPERIMENTAL DETAILS

Single crystals of SmFeAsO were grown using NaAs flux as described earlier.¹⁵ For the scattering measurements, an as-grown plate-like single crystal of approximate dimensions $2 \times 2 \times 0.1$ mm³ with a surface perpendicular to the c axis was selected. The XRMS and NRXMS experiments were performed on the ID20 beamline¹⁶ at the ESRF (European Synchrotron Radiation Facility) in Grenoble, France at the Sm L_2 , L_3 and Fe-K absorption edges and at the Fe K-edge at beamline P09 at the PETRA III synchrotron at DESY. The incident radiation was linearly polarized parallel to the horizontal scattering plane (π -polarization) and perpendicular to the vertical scattering plane (σ -polarization) for the ID20 and P09 beamlines, respectively. The spatial cross section of the beam was

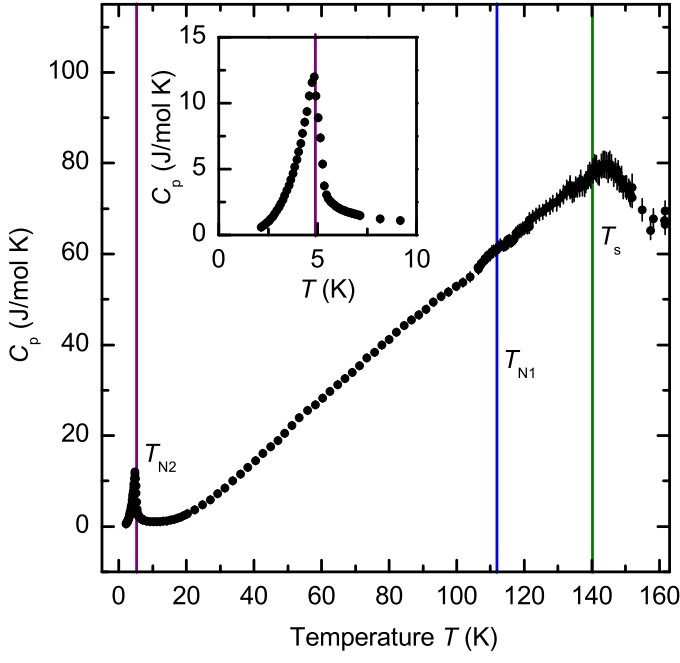


Figure 1: Temperature dependence of the specific heat. T_{N1} and T_{N2} are the spontaneous magnetic ordering temperatures of the Fe and Sm magnetic moments respectively. T_s is the structural phase transition temperature. Vertical lines are guides to the eye after x-ray diffraction measurements.

0.5 (horizontal) \times 0.5 (vertical) mm^2 for the ID20 while it was 0.2 (horizontal) \times 0.1 (vertical) mm^2 for P09. Au (2 2 0) was used at Sm L_2 edge and Cu (2 2 0) was used for both the Sm L_3 and Fe K absorption edges as a polarization and energy analyzer to suppress the charge and fluorescence background relative to the magnetic scattering signal. The sample was mounted at the end of the cold finger of a standard orange cryostat (at ID20), a vertical field cryomagnet (at ID20) and a displax refrigerator (at P09) with the ac plane coincident with the scattering plane. Measurements at ID20 were performed at temperatures between 1.6 and 150 K, while the lowest achievable temperature was 5 K at P09.

III. EXPERIMENTAL RESULTS

A. Macroscopic Characterizations

Figure 1 shows the heat capacity of a SmFeAsO single crystal, measured using a Quantum Design physical property measurement system (PPMS). Specific heat data shows phase transitions at 143.5 ± 2 K and 4.8 ± 0.2 K, respectively.

Figure 2(a) shows magnetic susceptibility of a SmFeAsO single crystal, measured using a Quantum Design SQUID magnetometer. Magnetic susceptibility shows a clear phase transition at 5 K. There is clear anomaly $\chi_{ab} > \chi_c$ over the whole temperature range. Figure 2(b) shows M - H curves at several temperatures for magnetic fields parallel to both c and ab planes, measured using a Quantum Design vibrating sam-

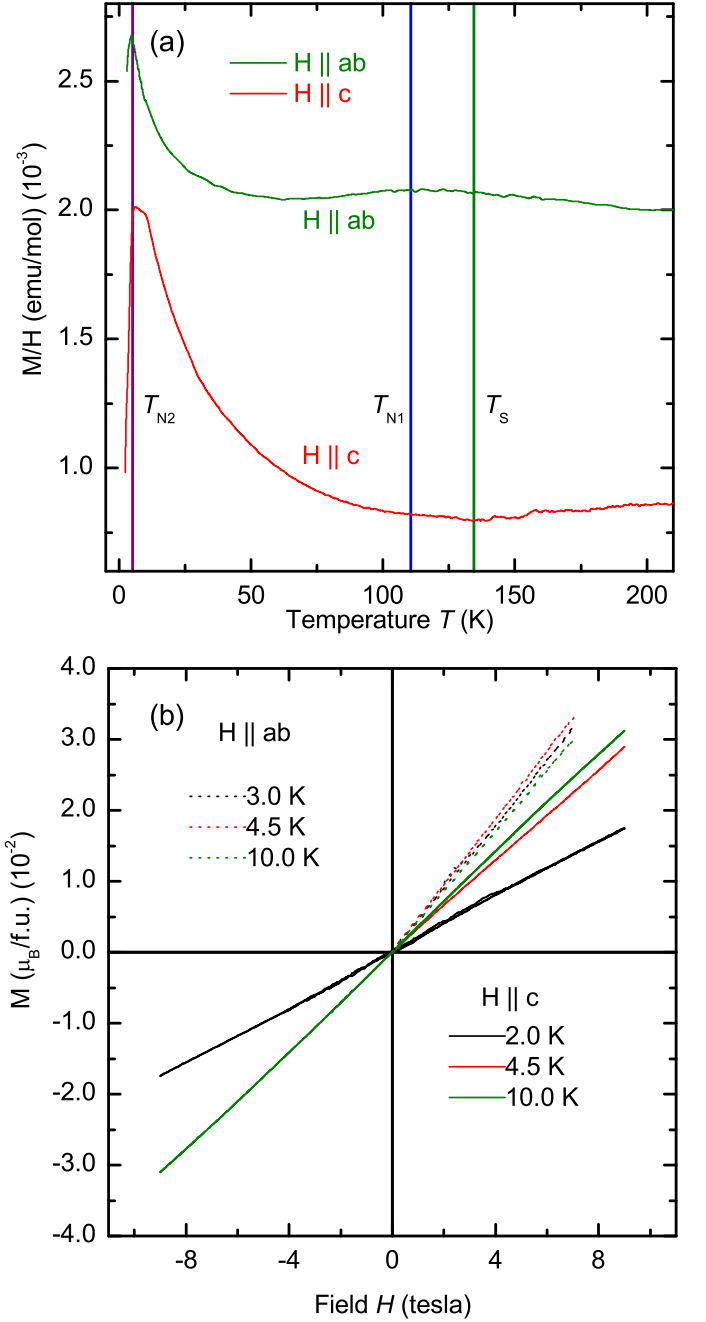


Figure 2: (a) Temperature dependence of the magnetic susceptibility measured on heating of the zero-field cooled sample in a field of 1 T. (b) M - H curves for magnetic fields parallel and perpendicular to the c direction at several temperatures.

ple magnetometer (VSM). Zero field intercept of M - H curves for both field directions places an upper limit of ferromagnetic contribution less than $1.7 \times 10^{-6} \mu_B/\text{f.u.}$ for all the temperatures measured.

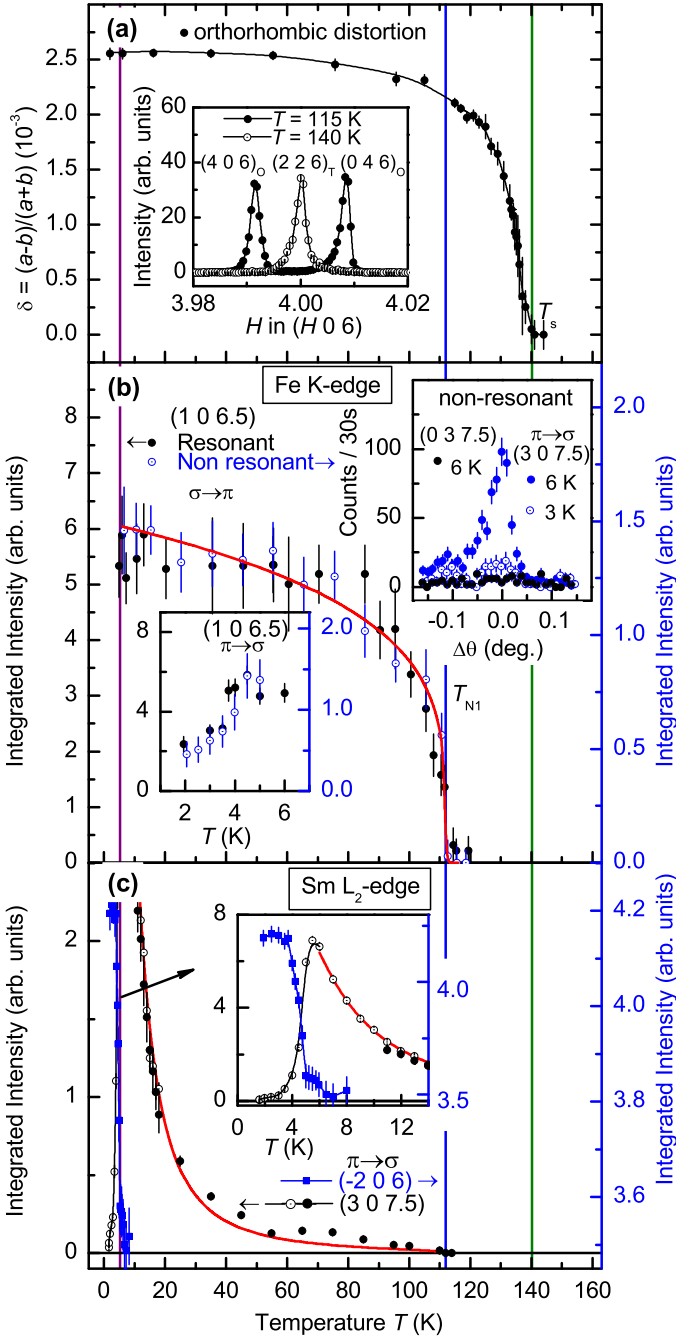


Figure 3: (a) Temperature dependence of the orthorhombic distortion. Inset shows $(\xi 0 0)_T$ scans through the $(4 0 6)_O$ reflection. (b) Temperature dependence of the (106.5) reflection measured in both resonant (at $E = 7.106$ keV which is 6 eV below the Fe K-edge energy of 7.112 keV) and non-resonant (100 eV below the Fe K-edge) conditions at P09 with a dispex. Lower inset shows temperature dependence of the (106.5) reflection measured using the cryomagnet. All other measurements below 5 K were performed using the orange cryostat. Upper inset shows rocking scans at the (307.5) and (037.5) reflections at selected temperatures. (c) Temperature dependencies of the (307.5) and (-206) reflections measured in resonant condition ($E = 7.314$ keV) at the Sm L_2 edge. Open (closed) circles represent measurements with (without) attenuation of the primary beam. Solid thin lines serve as guides to the eye while thick lines (red) show fit as described in the text.

B. Observation of resonant and non-resonant magnetic scattering and characterization of the transition temperatures

To determine whether there is a structural phase transition, as observed in powder SmFeAsO ,¹⁷ $(\xi \xi 0)_T$ scans were performed through the tetragonal (T) $(226)_T$ Bragg reflection as a function of temperature. As shown in the inset to Fig. 3(a), the $(226)_T$ Bragg reflection splits into orthorhombic (O) $(406)_O$ and $(046)_O$ Bragg reflections below $T_S = 140 \pm 1$ K. This splitting is consistent with the structural phase transition from space group $P4/nmm$ to $Cmme$. The orthorhombic distortion, δ ,^{17,18} increases with decreasing temperature without any noticeable change at the 5 K phase transition. We note that the transition temperature T_S is consistent with the peak observed in specific heat data. In the remainder of the paper, we will use orthorhombic crystallographic notation.

Below $T_{N1} = 110$ K, a magnetic signal was observed at the reciprocal lattice points characterized by the propagation vector $(10\frac{1}{2})$ when the x-ray energy was tuned through the Sm L_2 and Fe K-edges, indicating the onset of Sm and Fe magnetic order, respectively. Figure 3(b) shows a very similar temperature evolution of the non-resonant and the resonant signal at the Fe K-edge for the (106.5) reflection, supporting the magnetic origin of the resonant signal. Resonant signal was measured at the maximum in the resonant scattering ($E = 7.106$ keV) at the Fe K-edge while the non-resonant signal was measured approximately 100 eV below the Fe K edge. Temperature dependence of this reflection below 5 K (lower inset) together with rocking scans shown in the upper inset confirm that the iron magnetic order changes below 5 K. Figure 3(c) depicts the temperature evolution of the (307.5) and (-206) reflections measured at the Sm L_2 edge at resonance ($E = 7.314$ keV). At $T_{N2} = 5$ K, the intensity of the (307.5) reflection drops quickly to zero, and reappears at the position of the charge (-206) reflection, signaling a change in the magnetic order of Sm with the magnetic unit cell equal to the chemical unit cell. Here we note that all the measurements below 15 K require significant attenuation (transmission $\sim 10\%$ of the incident beam) of the beam to reduce sample heating.

To confirm the resonant magnetic behavior of the peaks, we performed energy scans at the Sm L_2 , L_3 and Fe K absorption edges as shown in Fig. 4. At 6 K, at the Sm L_2 edge we observed a dipole resonance peak approximately 2 eV above the absorption edge for both the (107.5) and (-206) reflections. We note that for the (-206) reflection charge and magnetic peak coincide. Therefore, measurement of magnetic signal which is five to six orders of magnitude weaker than the Thomson charge scattering requires significant reduction of the charge background. The charge background can be reduced significantly by a factor of $\cos^2 2\theta_{\text{analyzer}} \times \cos^2 2\theta_{\text{sample}}$ in the $\pi \rightarrow \sigma$ geometry for the reflections with the scattering angle ($2\theta_{\text{sample}}$) close to 90° .²¹ (-206) reflection with the scattering angles ($2\theta_{\text{sample}}$) of $\sim 86^\circ$ and $\sim 95^\circ$ at the Sm L_2 and Sm L_3 edges, respectively, fulfills these conditions. The charge signal is reduced by a factor of $\sim 7 \times 10^{-6}$ with the scattering angle of the analyzer ($2\theta_{\text{analyzer}}$) close to 92° for both the edges. Thus,

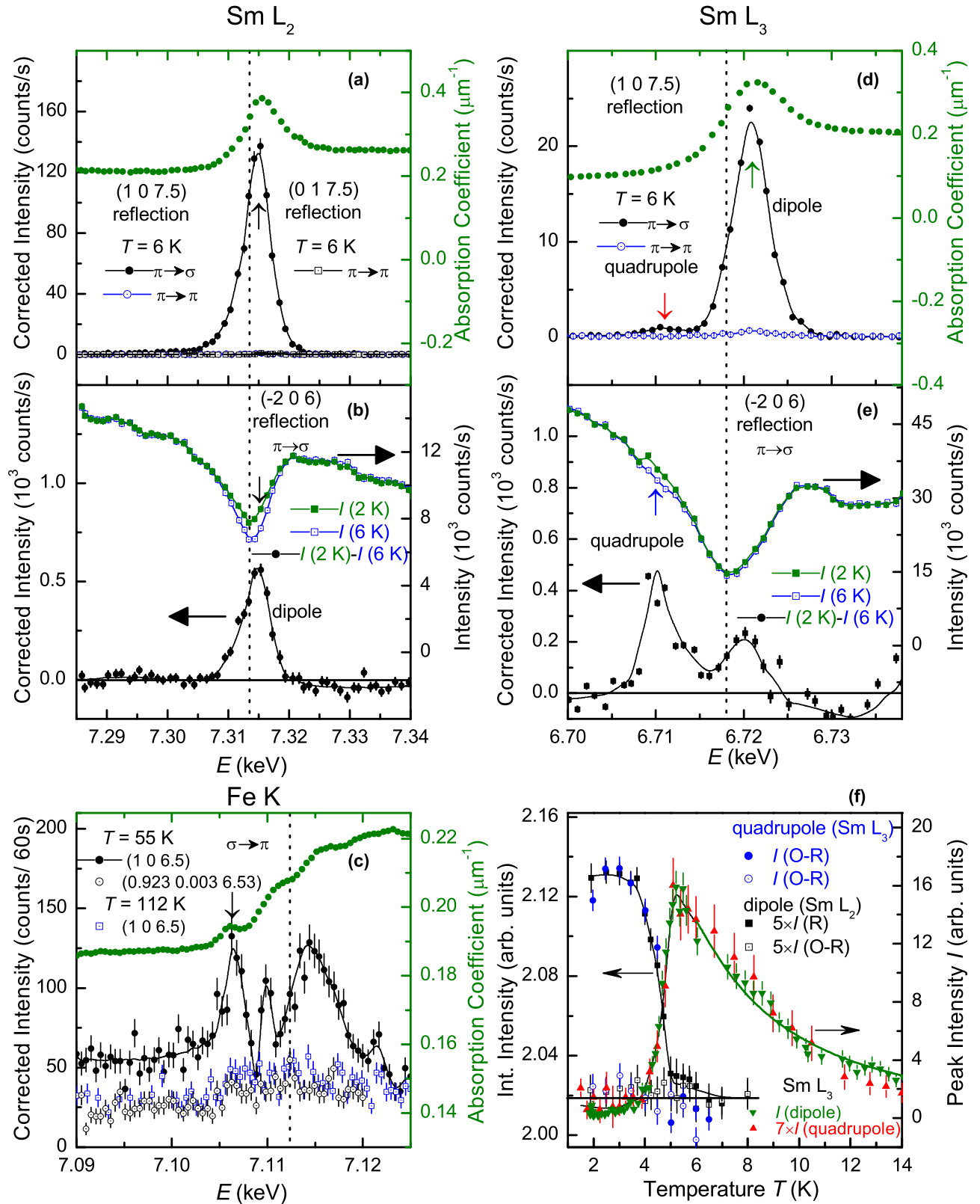


Figure 4: (a, d & b, e) Energy scans of the $(1\ 0\ 7.5)$, $(0\ 1\ 7.5)$ and $(-2\ 0\ 6)$ reflections and of the absorption coefficient at the Sm L_2 (left panel) and L_3 edges (right panel). The dashed lines depict the Sm L_2 and L_3 absorption edges as determined from the inflection point of the absorption coefficient. Absorption coefficient was calculated and the intensity was corrected following the recipe described in Refs. [19,20]. (c) Energy scans of the absorption coefficient and of the $(1\ 0\ 6.5)$ reflection below ($T = 55\text{ K}$, filled circles) and above ($T = 112\text{ K}$, open squares) T_{N1} and the measured background at $T = 55\text{ K}$ away from the magnetic Bragg peak (open circles). The dashed line depicts the Fe K -edge. (f) Comparison of the temperature dependences of the dipole and quadrupole resonances for the $(-2\ 0\ 6)$ and $(1\ 0\ 7.5)$ reflections, respectively. For the $(-2\ 0\ 6)$ reflection, integrated intensity was measured approximately 30 eV below (off-resonance, O-R) the observed resonance (R, $E = 6.710$ and 7.314 keV for the Sm L_3 and L_2 edges, respectively) to show the temperature dependence of the pure charge signal. The intensities have not been corrected for absorption. In (a-e) vertical arrows indicate the energies at which temperature dependences of the resonant signal was measured for Fig. 3(b-c) and Fig. 4(f). In (a-f) lines serve as guides to the eye.

measurement of magnetic signal seems feasible for the $(-2\ 0\ 6)$ reflection in the $\pi \rightarrow \sigma$ geometry. Figure 4(b) shows energy scans through the $(-2\ 0\ 6)$ reflection at 2 and 6 K. Subtraction of the energy scan at 6 K from 2 K shows a pronounced resonance feature at the same energy as that observed for the charge forbidden $(1\ 0\ 7.5)$ reflection. Similar energy scans were performed at the Sm L_3 edge and are shown in Fig. 4 (d-e). In addition to the dipole feature observed at the L_2 edge, quadrupole feature appear approximately 6 eV below the Sm L_3 edge. We note that the change in the energy spectra from the Sm L_2 to the L_3 edge is consistent with the observed resonance in another intermetallic compound containing Sm.²²

Figure. 4(c) shows the energy scan through the Fe K-edge. Several features are observable in the energy spectrum: (a) Resonant features at and above $E = 7.106$ keV and (b) an energy independent non-resonant signal for energies below the resonant features. The non-resonant signal is about a factor of 2.5 smaller than the resonant signal. The overall energy spectrum is similar to that observed in previous XRMS measurements in the $\sigma \rightarrow \pi$ scattering channel at the transition metal K-edges for the BaFe_2As_2 ²³, $\text{Ce}(\text{Co}_{0.07}\text{Fe}_{0.97})_2$ ²⁰ and NiO ²⁴ compounds. It is noteworthy that, the pre-edge sharp resonant feature observed at $E = 7.106$ keV for SmFeAsO is also present in all of the above mentioned compounds. It appears at an energy corresponding to the pre-edge hump observed in the respective absorption/fluorescence spectrum. The broad resonant feature above $E = 7.106$ keV is also present in all the above compounds, however, it's relative intensity compared to the sharp feature varies from one compound to another.

Further confirmation that the dipole and quadrupole resonances at the L_2 and L_3 edges are magnetic is obtained from the same temperature dependence of the dipole and quadrupole resonances as shown in Fig. 4(f) for both the $(-2\ 0\ 6)$ and $(1\ 0\ 7.5)$ reflections. Since the quadrupole signal is directly related to the ordering of the $4f$ moments, the similarity of the temperature dependences of both resonances implies that both the dipole and quadrupole resonances are purely magnetic.

C. Magnetic structure in the temperature range $5\text{ K} \leq T \leq 110\text{ K}$

We now turn to the determination of the magnetic moment configuration for the Sm moments in the temperature range $T_{N2} \leq T \leq T_{N1}$. For the crystallographic space group $Cmme$, and propagation vector of the form $(1\ 0\ \frac{1}{2})$, six independent magnetic representations (MRs) are possible.²⁵ All the MRs along with the calculated intensities for different polarization geometries are listed in Table I. Among all the MRs, Γ_8 (F) and Γ_1 (AF) MRs allow magnetic moment along a , Γ_2 (F) and Γ_7 (AF) along b and, Γ_4 (F) and Γ_5 (AF) along c direction, respectively. Here, F and AF denotes ferro and anti-ferromagnetic alignment between Sm(1) and Sm(2) moments, respectively (see Fig. 5(b)). For a second-order phase transition, Landau theory predicts that only one of the six above mentioned MRs is realized at the phase transition.²⁵ We note that the $\pi \rightarrow \pi$ scattering geometry is sensitive only to the

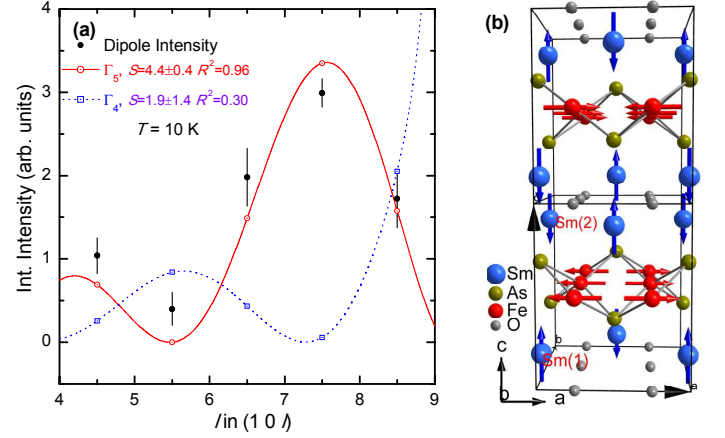


Figure 5: (a) l dependence of the integrated intensity at the Sm L_2 edge along with the fits for the $(1\ 0\ \frac{l}{2})$ reflections. Open symbols are the calculated intensities. Lines serve as guides to the eye. (b) Proposed magnetic structure in the temperature range $5\text{ K} \leq T \leq 110\text{ K}$

moment perpendicular to the scattering plane for the dipole resonance.²⁶ Since, no magnetic signal was observed at the $(0\ 1\ 7.5)$ (sensitive to Γ_1 and Γ_8) and $(1\ 0\ 7.5)$ (sensitive to Γ_2 and Γ_7) reflections in the $\pi \rightarrow \pi$ scattering channel at the Sm L_2 edge (see Fig. 4(a, d)), we can exclude the moment in the a and b directions and hence, the MRs Γ_1 , Γ_8 , Γ_2 and Γ_7 . To differentiate between the MRs Γ_4 and Γ_5 (moment along the c direction), the integrated intensities for a series of $(1\ 0\ \frac{l}{2})$ reflections were measured (see Fig. 5(a)) and compared with the calculated intensity as outlined below. The intensity for a particular reflection can be written as:

$$I = SAL|F_m|^2 \quad (1)$$

where S is arbitrary scaling factor, $A = \frac{\sin(\theta+\alpha)}{\sin\theta \cos\alpha}$ is the absorption correction, $L = \frac{1}{\sin 2\theta}$ is the Lorentz factor. Here, α is the angle that the scattering vector $\mathbf{Q} (= \mathbf{k}_f - \mathbf{k}_i)$ makes with the crystallographic c direction perpendicular to the surface of the sample and, θ is half of the scattering angle. α is positive/negative for larger/smaller angles for the outgoing beam with respect to the sample surface. $|F_m|$ is the modulus of the magnetic structure factor. The magnetic structure factor F_m for the $(h\ k\ l)$ reflections can be written as:

$$F_m = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad (2)$$

The summation is over all the magnetic atoms in the unit cell. f_j is the resonant/non-resonant magnetic scattering amplitude which is listed for different polarization geometries by Hill and McMorrow for XRMS²⁶ and by M. Blume and D. Gibbs for NRXMS²⁷. In particular, f_j depends on the polarization geometry as well as the moment direction. x_j , y_j and z_j are the atomic position of the j th atom within the unit cell. The angular dependence of the magnetic structure factor originates from the magnetic scattering amplitude f_j . For dipole resonance and for the $\pi \rightarrow \sigma$ geometry, $f_j \propto \mathbf{k}_i \cdot \boldsymbol{\mu}$,^{26,28} where \mathbf{k}_i

and μ are the wave vectors of the incoming photons and the magnetic moment, respectively. For the dipole resonance, and for the reflections of the type $(1\ 0\ \frac{1}{2})$, $|F_m|^2$ is proportional to $\sin^2(2\pi z l) \sin^2(\theta + \alpha)$ and $\cos^2(2\pi z l) \sin^2(\theta + \alpha)$ for the Γ_4 and Γ_5 MRs, respectively. $z = 0.137$ is atomic position of Sm moments within the unit cell.¹⁷ While $\sin^2(2\pi z l)/\cos^2(2\pi z l)$ term comes from the relative orientation of the magnetic moment within the magnetic unit cell, the term $\sin^2(\theta + \alpha)$ comes from the dot product between \mathbf{k}_i and μ [$(90^\circ - \theta - \alpha)$ is the angle between \mathbf{k}_i and μ]. We note, that there is only one free parameter for the dipole intensity (see Eqn. 1), namely the arbitrary scaling factor S . Figure 5(a) shows a fit to the observed intensities for the two above mentioned MRs. Since the model calculation with the magnetic moment in the Γ_5 MR closely agrees with the observed intensity, we conclude that the magnetic Sm moments are arranged according to the MR Γ_5 .

For the determination of the MR for the Fe moments, the non-resonant signal was measured at 15 K. Similar representation analysis provides six possible MRs for the magnetic order of Fe. All the MRs along with the calculated intensities for different polarization geometries are listed in Table II. Among all the MRs, Γ_5 and Γ_6 MRs allow magnetic moment along a , Γ_3 and Γ_4 along b and Γ_1 and Γ_2 along c direction, respectively. Among the two MRs for a particular moment direction, the first one represents F alignment of the magnetic moments along b and AF alignment along a while the second one represents exactly the opposite alignment in the respective directions. Γ_2 , Γ_3 , Γ_4 and Γ_6 MRs can be excluded from the fact that finite intensity was observed for the $(1\ 0\ 6.5)$ reflection in the $\pi \rightarrow \sigma$ geometry (see Table II). Zero intensities for the $(0\ 3\ 7.5)$ reflection in the $\pi \rightarrow \sigma$ geometry (see inset of Fig. 3(b)) and of the $(1\ 0\ 6.5)$ reflection in the $\pi \rightarrow \pi$ channel are also consistent with the absence of Γ_4 and Γ_3 MRs, respectively. Finite intensity of the $(1\ 0\ 6.5)$ reflection in the $\pi \rightarrow \sigma$ channel implies that the moments are within the a - c scattering plane i.e. Γ_1 and Γ_5 are the possible MRs. We measured the off-specular reflections $(3\ 0\ 7.5)$ and $(\bar{3}\ 0\ 7.5)$ to determine the moment direction. The angular dependence of the non-resonant magnetic scattering cross section for the $\pi \rightarrow \sigma$ geometry, $f_j = -2 \sin^2 \theta \mathbf{k}_f \cdot \mathbf{S}$ (assuming spin only magnetic moment of iron),²⁷ is different for these two reflections providing strong sensitivity to the moment direction. \mathbf{k}_f and \mathbf{S} are the wave vectors of the outgoing photons and the spin magnetic moment, respectively. The ratio can be written as:

$$\frac{I(h\ 0\ \frac{1}{2})}{I(\bar{h}\ 0\ \frac{1}{2})} = \frac{\sin(\theta - \alpha) \cos^2(\theta - \alpha)}{\sin(\theta + \alpha) \cos^2(\theta + \alpha)} \quad (3)$$

The calculated ratio $I(3\ 0\ 7.5)/I(\bar{3}\ 0\ 7.5)$ amounts to 5.2 and 0.35 for moments along the a and c directions, respectively. The experimentally determined ratio 6.5 ± 0.9 confirms that the moments are in the a direction, i.e. the MR is Γ_5 . We note that this is the same MR as that of Sm, which is expected if there is significant coupling between the two magnetic sublattices. Arrangements of the magnetic moments according to the MR Γ_5 is shown in Fig. 5(b).

Table I: Basis vectors for the space group $Cmme$ with $\mathbf{k}_{17} = (0, 1, .5)$. The decomposition of the magnetic representation for the Sm site $(0, .25, .137)$ is $\Gamma_{Mag} = 1\Gamma_1^1 + 1\Gamma_2^1 + 0\Gamma_3^1 + 1\Gamma_4^1 + 1\Gamma_5^1 + 0\Gamma_6^1 + 1\Gamma_7^1 + 1\Gamma_8^1$. The atoms of the nonprimitive basis are defined according to 1: $(0, .25, .137)$, 2: $(0, .75, .863)$. Lattice parameters of the orthorhombic crystal at 100 K¹⁷: $a = 5.5732\ \text{\AA}$, $b = 5.5611\ \text{\AA}$, $c = 8.4714\ \text{\AA}$.

| IR | Atom | BV components | | | Magnetic Intensity | | | |
|------------|------|-------------------|-------------------|-------------------|--------------------------|-----------------------|--------------------------|-----------------------|
| | | $m_{\parallel a}$ | $m_{\parallel b}$ | $m_{\parallel c}$ | $(h\ 0\ \frac{1}{2})$ | $(0\ k\ \frac{1}{2})$ | $(0\ k\ \frac{1}{2})$ | $(0\ k\ \frac{1}{2})$ |
| | | | | | $\pi \rightarrow \sigma$ | $\pi \rightarrow \pi$ | $\pi \rightarrow \sigma$ | $\pi \rightarrow \pi$ |
| Γ_1 | 1 | 1 | 0 | 0 | Yes | No | No | Yes |
| | 2 | -1 | 0 | 0 | | | | |
| Γ_2 | 1 | 0 | 1 | 0 | No | Yes | Yes | No |
| | 2 | 0 | 1 | 0 | | | | |
| Γ_4 | 1 | 0 | 0 | 1 | Yes | No | Yes | No |
| | 2 | 0 | 0 | 1 | | | | |
| Γ_5 | 1 | 0 | 0 | 1 | Yes | No | Yes | No |
| | 2 | 0 | 0 | -1 | | | | |
| Γ_7 | 1 | 0 | 1 | 0 | No | Yes | Yes | No |
| | 2 | 0 | -1 | 0 | | | | |
| Γ_8 | 1 | 1 | 0 | 0 | Yes | No | No | Yes |
| | 2 | 1 | 0 | 0 | | | | |

Table II: Basis vectors for the space group $Cmme$ with $\mathbf{k}_{17} = (0, 1, .5)$. The decomposition of the magnetic representation for the Fe site $(.75, 0, .5)$ is $\Gamma_{Mag} = 1\Gamma_1^1 + 1\Gamma_2^1 + 1\Gamma_3^1 + 1\Gamma_4^1 + 1\Gamma_5^1 + 1\Gamma_6^1 + 0\Gamma_7^1 + 0\Gamma_8^1$. The atoms of the nonprimitive basis are defined according to 1: $(.75, 0, .5)$, 2: $(.75, .5, .5)$.

| IR | Atom | BV components | | | Magnetic Intensity | | | |
|------------|------|-------------------|-------------------|-------------------|--------------------------|-----------------------|--------------------------|-----------------------|
| | | $m_{\parallel a}$ | $m_{\parallel b}$ | $m_{\parallel c}$ | $(h\ 0\ \frac{1}{2})$ | $(0\ k\ \frac{1}{2})$ | $(0\ k\ \frac{1}{2})$ | $(0\ k\ \frac{1}{2})$ |
| | | | | | $\pi \rightarrow \sigma$ | $\pi \rightarrow \pi$ | $\pi \rightarrow \sigma$ | $\pi \rightarrow \pi$ |
| Γ_1 | 1 | 0 | 0 | 1 | Yes | No | No | No |
| | 2 | 0 | 0 | 1 | | | | |
| Γ_2 | 1 | 0 | 0 | 1 | No | No | Yes | No |
| | 2 | 0 | 0 | -1 | | | | |
| Γ_3 | 1 | 0 | 1 | 0 | No | Yes | No | No |
| | 2 | 0 | 1 | 0 | | | | |
| Γ_4 | 1 | 0 | 1 | 0 | No | No | Yes | No |
| | 2 | 0 | -1 | 0 | | | | |
| Γ_5 | 1 | 1 | 0 | 0 | Yes | No | No | No |
| | 2 | 1 | 0 | 0 | | | | |
| Γ_6 | 1 | 1 | 0 | 0 | No | No | No | Yes |
| | 2 | -1 | 0 | 0 | | | | |

D. Temperature dependence of the magnetic intensity in the temperature range $5\ \text{K} \leq T \leq 110.0\ \text{K}$

Although the ordering temperatures are the same for both the Fe and Sm sublattices, the order parameters are qualitatively different as can be seen from Fig. 3(b-c). Particularly, the order parameter for the Sm moment is quite unusual. Very similar temperature dependence of the Ce sublattice magnetization in CeFeAsO has been obtained indirectly using muon spin relaxation measurements.¹⁰ With reference to other systems this unusual behavior can be explained with a ground-state doublet crystal-field level, split by an exchange field.^{29,30} The Kramer's Sm^{3+} ions in SmFeAsO are at the positions of

local point symmetry C_{2v} and, therefore, must have a doublet ground-state. At low temperatures only the ground-state doublet is appreciably populated because the energy difference between the ground-state and the next crystal electric-field levels, in general, is large, and of the order of 17 meV in case of CeFeAsO.³¹ Taking into account only the ground-state doublet and a splitting, $\Delta(T)$, we can write:

$$m_z^{Sm}(T) = \frac{g_J \mu_B}{2} \tanh\left[\frac{\Delta(T)}{2k_B T}\right] \quad (4)$$

where $\Delta(T) = g_J \mu_B B_z^{eff}(T)$ is the splitting of the ground state doublet by the effective field produced by the Fe sublattice. $g_J = \frac{2}{7}$ is the Landé g factor of the free Sm^{3+} and μ_B is the Bohr magneton. The effective field should be proportional to the ordered magnetic moment of Fe, and can be written as:

$$B_z^{eff}(T) = B_0 \left(1 - \frac{T}{T_N}\right)^\beta \quad (5)$$

Since the observed intensity is proportional to the square of the ordered magnetic moment ($I = A m^2$), T_N ($=110 \pm 1$ K) and β ($=0.112 \pm 0.008$) can be extracted from a fit to the integrated intensity for the (106.5) reflection in Fig. 3(b). A fit to the temperature dependence of the (307.5) reflection in Fig. 3(c) over the whole temperature range gives $B_0 = (56.4 \pm 1.9)$ Tesla and corresponding $\Delta(T=0) = (0.93 \pm 0.03)$ meV. We note that the value of B_0 characterizing the strength of interaction between the two sublattices is comparable or even higher than the value for Ce-Fe interaction in CeFeAsO.^{10,32} The value of $\Delta = 0.93$ meV is comparable to the ground state splitting of Ce crystal electric field levels of 0.9 meV in CeFeAsO, measured using inelastic neutron scattering.³¹

E. Magnetic structure below $T \leq 5.0$ K

For the low temperature phase ($T \leq 5.0$ K), the determination of the magnetic structure of the Sm subsystem is considerably more difficult due to the overlap of the magnetic intensity with the charge intensity. Magnetization measurements with magnetic fields along the c direction and in the ab plane exclude ferromagnetic arrangement in the respective direction/plane, see Fig. 2(b). There remain three antiferromagnetic representations along a , b , and c directions. The relative change in magnetization below 5 K is much more pronounced for a magnetic field applied along the c direction than in the ab plane (see Fig. 2(a)). Therefore, we conclude that the Sm moments are aligned along the c direction below 5 K, which is in agreement with recent neutron scattering measurements.¹⁴

To determine the magnetic structure of the Fe moments below $T = 5$ K, a number of possible propagation vectors suggested for the RFeAsO family¹⁰, (100.5), (100), (0.500.5) and (000.5) were checked by rocking scans with counting time (~ 3 min/data point) a factor of three larger than other measurements at 2 K. Measurements were performed in both the $\pi \rightarrow \sigma$ and $\pi \rightarrow \pi$ channels to exclude possible re-orientation of the magnetic moments from a to b direction.

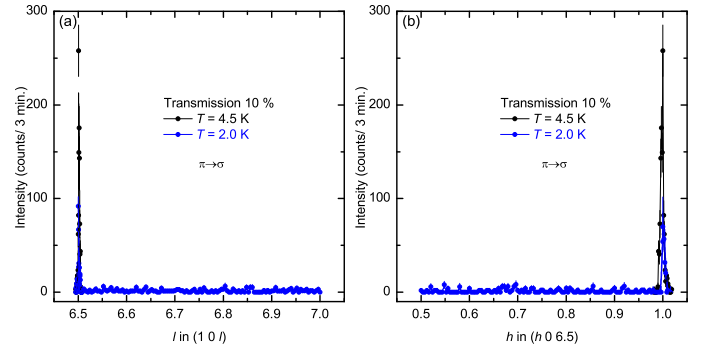


Figure 6: (a & b) l and h scans through the (106.5) reflection. 10 % of the incident beam was used to reduce the sample heating. For comparison, scans at $T = 4.5$ K is plotted together with scans taken at $T = 2.0$ K. We noticed that the sample heating is much more in the cryomagnet than in the orange cryostat. The remaining intensity at $T = 2$ K is due to the residual sample heating in the cryomagnet.

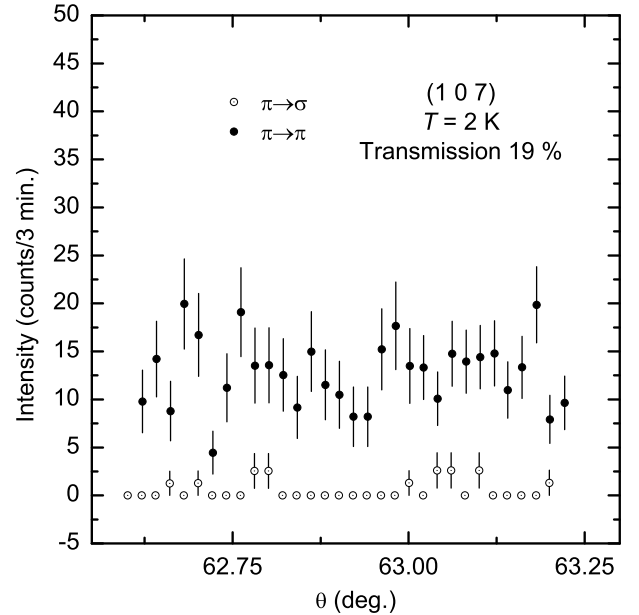


Figure 7: Rocking scans through the (107) reflection in both the $\pi \rightarrow \sigma$ and $\pi \rightarrow \pi$ channels. Higher background in the $\pi \rightarrow \pi$ channel is mainly due to the less suppression of the fluorescence background.

Additionally, long scans along h and l directions for the (106.5) reflections were performed to exclude possible incommensurate order in the respective directions, see Fig. 6. However, no signal was observed for the above measurements. Its magnetic structure with the same propagation vector as that of Sm implies a Néel type in-plane structure which is impossible to check with hard x-rays given the weakness of the resonant/non-resonant signal and overlap of the magnetic signal with the charge signal. In NdFeAsO a change in the coupling along the c axis (AFM to FM) has been observed upon the spontaneous order of Nd.¹¹ However, this is not the case here, as confirmed by the absence of the scattering signal

at the (1 0 7) reflection as shown in Fig. 7. The absence of the scattering signal in the positions mentioned above indicates that the in-plane as well as out-of plane correlations are modified upon the spontaneous ordering of Sm. This observation is unique among the $R\text{FeAsO}$ family and indicate an intricate interplay between the two sublattices. Here we note that the rare earth sites project onto the centers of the Fe plaquettes and thus isotropic interactions between the two vanishes by symmetry. Hence, anisotropic exchange interactions play a major role in determining the spin structure of the Fe sublattice and should be studied theoretically to understand the magnetism in the $R\text{FeAsO}$ family.

IV. CONCLUSION

In summary, using XRMS and NRXMS we found that between 110 K and 5 K, the Sm moments are aligned in the c

direction while Fe moments are aligned in the a direction according to the same MR Γ_5 and the propagation vector ($1\ 0\ \frac{1}{2}$). Modeling of the temperature dependence indicates that the Sm moments are induced by the exchange field of the Fe moments. Below 5 K, the magnetic order of both sublattices change to a different magnetic structure, indicating an intricate interplay between the two magnetic sublattices. Our finding of an intricate interplay between the magnetism of Sm and Fe in the SmFeAsO compound sheds new light on the currently debated importance of the R -Fe interaction in the family of iron based superconductors.

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- ¹ Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
- ² X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature **453**, 761 (2008).
- ³ C. Wang, L. Li, S. Chi, Z. Zhu, Z. Ren, Y. Li, Y. Wang, X. Lin, Y. Luo, S. Jiang, et al., Europhys. Lett. **83**, 67006 (2008).
- ⁴ Z.-A. Ren, J. Yang, W. Lu, W. Yi, X.-L. Shen, Z.-C. Li, G.-C. Che, X.-L. Dong, L.-L. Sun, F. Zhou, et al., Europhys. Lett. **82**, 57002 (2008).
- ⁵ H. Kito, H. Eisaki, and A. Iyo, J. Phys. Soc. Jpn. **77**, 063707 (2008).
- ⁶ J.-W. G. Bos, G. B. S. Penny, J. A. Rodgers, D. A. Sokolov, A. D. Huxley, and J. P. Attfield, Chem. Commun. **31**, 3634 (2008).
- ⁷ M. Tropeano, A. Martinelli, A. Palenzona, E. Bellingeri, E. Galleani d'Agliano, T. D. Nguyen, M. Affronte, and M. Putti, Phys. Rev. B **78**, 094518 (2008).
- ⁸ L. Ding, C. He, J. K. Dong, T. Wu, R. H. Liu, X. H. Chen, and S. Y. Li, Phys. Rev. B **77**, 180510 (2008).
- ⁹ A. J. Drew, C. Niedermayer, P. J. Baker, F. L. Pratt, S. J. Blundell, T. Lancaster, R. H. Liu, G. Wu, X. H. Chen, I. Watanabe, et al., Nat. Mater. **8**, 310 (2009).
- ¹⁰ H. Maeter, H. Luetkens, A. G. Pashkevich, A. Kwadrin, R. Khasanov, A. Amato, A. Gusev, K. V. Lamonova, D. A. Chervinskii, R. Klingeler, et al., Phys. Rev. B **80**, 094524 (2009).
- ¹¹ W. Tian, W. Ratcliff, M. G. Kim, J.-Q. Yan, P. A. Kienzle, Q. Huang, B. Jensen, K. W. Dennis, R. W. McCallum, T. A. Lo-grasso, et al., Phys. Rev. B **82**, 060514 (2010).
- ¹² J. Herrero-Martín, V. Scagnoli, C. Mazzoli, Y. Su, R. Mittal, Y. Xiao, T. Brueckel, N. Kumar, S. K. Dhar, A. Thamizhavel, et al., Phys. Rev. B **80**, 134411 (2009).
- ¹³ Y. Xiao, Y. Su, M. Meven, R. Mittal, C. M. N. Kumar, T. Chatterji, S. Price, J. Persson, N. Kumar, S. K. Dhar, et al., Phys. Rev. B **80**, 174424 (2009).
- ¹⁴ D. H. Ryan, J. M. Cadogan, C. Ritter, F. Canepa, A. Palenzona, and M. Putti, Phys. Rev. B **80**, 220503 (2009).
- ¹⁵ J.-Q. Yan, S. Nandi, J. L. Zarestky, W. Tian, A. Kreyssig, B. Jensen, A. Kracher, K. W. Dennis, R. J. McQueeney, A. I. Goldman, et al., Appl. Phys. Lett. **95**, 222504 (2009).
- ¹⁶ L. Paolasini, C. Detlefs, C. Mazzoli, S. Wilkins, P. P. Deen, A. Bombardi, N. Kernavanois, F. de Bergevin, F. Yakhov, J. P. Valade, et al., J. Synchrotron Radiat. **14**, 301 (2007).
- ¹⁷ A. Martinelli, A. Palenzona, C. Ferdeghini, M. Putti, and H. Emerich, J. Alloy. Compd. **477**, L21 (2009).
- ¹⁸ S. Nandi, M. G. Kim, A. Kreyssig, R. M. Fernandes, D. K. Pratt, A. Thaler, N. Ni, S. L. Bud'ko, P. C. Canfield, J. Schmalian, et al., Phys. Rev. Lett. **104**, 057006 (2010).
- ¹⁹ M. K. Sanyal, D. Gibbs, J. Bohr, and M. Wulff, Phys. Rev. B **49**, 1079 (1994).
- ²⁰ L. Paolasini, S. Di Matteo, P. P. Deen, S. Wilkins, C. Mazzoli, B. Detlefs, G. Lapertot, and P. Canfield, Phys. Rev. B **77**, 094433 (2008).
- ²¹ J. W. Kim, A. Kreyssig, P. Ryan, E. Mun, P. C. Canfield, and A. I. Goldman, Appl. Phys. Lett. **90**, 202501 (2007).
- ²² C. Adriano, R. Lora-Serrano, C. Giles, F. de Bergevin, J. C. Lang, G. Srajer, C. Mazzoli, L. Paolasini, and P. G. Pagliuso, Phys. Rev. B **76**, 104515 (2007).
- ²³ M. G. Kim, A. Kreyssig, Y. B. Lee, J. W. Kim, D. K. Pratt, A. Thaler, S. L. Bud'ko, P. C. Canfield, B. N. Harmon, R. J. McQueeney, et al., Phys. Rev. B **82**, 180412 (2010).
- ²⁴ W. Neubeck, C. Vettier, F. de Bergevin, F. Yakhov, D. Mannix, O. Bengone, M. Alouani, and A. Barbier, Phys. Rev. B **63**, 134430 (2001).
- ²⁵ A. S. Wills, Physica B **276-278**, 680 (2000).
- ²⁶ J. P. Hill and D. F. McMorrow, Acta Cryst. **A52**, 236 (1996).
- ²⁷ M. Blume and D. Gibbs, Phys. Rev. B **37**, 1779 (1988).
- ²⁸ T. Brückel, D. Hupfeld, J. Stremper, W. Caliebe, K. Mattenberger, A. Stunault, N. Bernhoeft, and G. J. McIntyre, Eur. Phys. J. B **19**, 475 (2001).
- ²⁹ R. Sachidanandam, T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B **56**, 260 (1997).
- ³⁰ S. Nandi, A. Kreyssig, L. Tan, J. W. Kim, J. Q. Yan, J. C. Lang, D. Haskel, R. J. McQueeney, and A. I. Goldman, Phys. Rev. Lett. **100**, 217201 (2008).
- ³¹ S. Chi, D. T. Adroja, T. Guidi, R. Bewley, S. Li, J. Zhao, J. W. Lynn, C. M. Brown, Y. Qiu, G. F. Chen, et al., Phys. Rev. Lett. **101**, 217002 (2008).
- ³² A. Jesche, C. Krellner, M. de Souza, M. Lang, and C. Geibel, New J. Phys. **11**, 103050 (2009).